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(54) Title: AN AMIDO TRANSITION METAL COMPOUND AND A CATALYST SYSTEM FOR THE PRODUCTION OF ISOTACTIC POLYPROPYLENE
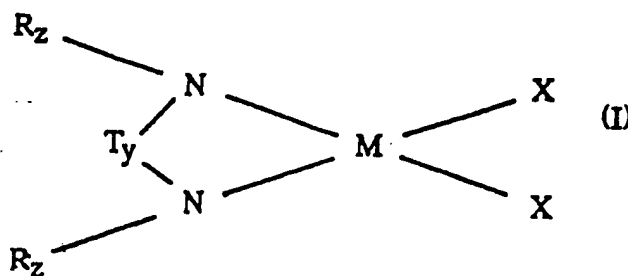
(57) Abstract

Bridged and unbridged amido transition metal compounds of the Group IV-B metals are disclosed. They are represented by general formula (I) wherein: "y" is 1 denoting the presence of a bridging group T between nitrogen atoms; "Z" is - y; "M" is zirconium, hafnium or titanium; "N" is a nitrogen atom having three substituents; each "X" is, independently, any univalent anionic ligand such as a halide, hydride, substituted or unsubstituted C_1-C_{30} hydrocarbyl, alkoxide, aryloxide, amide, arylamide, phosphide, or arylphosphide; "T" is a covalent bridging group selected from the group consisting of unsubstituted hydrocarbyl and substituted hydrocarbyls containing a Group IV-A or VI-A element; and each "R" is, independently, a radical selected from the group consisting of singly branched hydrocarbyl radicals having between 4 and 30 carbon atoms, multiply branched hydrocarbyl radicals having between 4 and 30 carbon atoms, halogen radicals, amido radicals, phosphido radicals, silyl radicals, alkoxy radicals, alkylborido radicals, C_1-C_{30} hydrocarbyl-substituted Group IV-A metalloid radicals; and substituted C_1-C_{30} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amino radical, a phosphido radical, an alkoxy radical or any other radical containing a Lewis acidic or basic functionality. These compounds may be used in a catalyst system comprising the amido transition metal compound and an alumoxane. Also disclosed is a process using the catalyst system for the production of high molecular weight polyolefins and, particularly, high molecular weight isotactic polypropylene.

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AN AMIDO TRANSITION METAL COMPOUND AND A
CATALYST SYSTEM FOR THE PRODUCTION OF
ISOTACTIC POLYPROPYLENE.

SPECIFICATION

FIELD OF THE INVENTION

This invention relates to certain bridged and
unbridged amido transition metal compounds of the Group
IV-B metals, to a catalyst system comprising an amido
transition metal compound and an alumoxane, and to a
process using the catalyst system for the production of
high molecular weight polyolefins and, particularly, high
molecular weight isotactic polypropylene.

BACKGROUND OF THE INVENTION

The various compounds that are derived from the
polymerization of α-olefins show huge differences in
their chemical and physical properties. These
differences reflect differences in molecular structure,
some of which are inherent in the use of a particular
monomer or monomer combination, and some of which result
from a pattern, or lack thereof, in how the monomers are
combined. It is inherent that polymers of α-olefins
having 3 or more carbon atoms will have pendant
hydocarbyl groups attached to the polymer backbone chain.
However, the stereochemical arrangement of these
hydrocarbyl groups is a consequence of the interaction of
monomer, catalyst and coordinated polymer during
polymerization. Any pendant hydrocarbyl group may be
said to lï on ne side f a plan defin d by th carbon
atoms of the polymer backbon in an id alized el ngated
configurati n.

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As previously alluded to, the physical properties exhibited by a particular olefin polymer of a particular molecular weight are determined in major part by the arrangement of these hydrocarbyl groups along the polymer backbone. Strong polymers tend to be stereochemically regular, meaning the adjacent hydrocarbyl groups reside on the same side of the polymer backbone or switch at fairly regular intervals. Either arrangement facilitates crystalization thus lending ridgidity and strength to the the solidified polymer.

Other critical determinants of the properties which a polymer will exhibit are the type and relative concentration of monomers and comonomers, the weight average molecular weight (M_w) of the polymer molecules comprising the resin bulk, the molecular weight distribution (MWD) and the composition distribution of the resin. For end use applications which require high strength and low creep, the M_w of such a resin must generally be in excess of 100,000.

Five types of stereoregularity, or tacticity, have been characterized: atactic, normal isotactic, isotactic stereoblock, syndiotactic, and hemiisotactic. Although all of these stereoregular configurations have been primarily demonstrated in the case of polypropylene, in theory each is equally possible for polymers comprised of any olefin, cyclic olefin or internal olefin, having 3 or more carbon atoms.

Atactic polyolefins are those wherein the hydrocarbyl groups pendent to the polymer molecule backbone assume no regular order in space with reference to the backbone. This random structure is represented by a polymer backbon of alt rnating m thylene and methine carbons, with randomly oriented branch s substituting the m thine carbons. The methine carbons randomly have R and S c nfigurati ns, creating adjac nt pairs either of lik

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configuration (a "meso" or "m" dyad) or of unlike
configuration (a "racemic" or "r" dyad). The atactic
form of a polymer contains approximately equal fractions
of meso and racemic dyads. Since atactic polyolefins
exhibit no regular order or repeating unit configurations
in the polymer chain, they are amorphous materials.
Atactic polyolefins exhibit little if any crystallinity,
hence they are generally unsuitable for high strength
applications regardless of the weight average molecular
weight of the resin.

Isotactic polyolefins are those wherein the pendent
hydrocarbyl groups are ordered in space to the same side
or plane of the polymer backbone chain. Using isotactic
polypropylene as an example, the isotactic structure is
typically described as having the pendent methyl groups
attached to the ternary carbon atoms of successive
monomeric units on the same side of a hypothetical plane
through the carbon backbone chain of the polymer, e.g.,
the methyl groups are all above or below the plane as
shown below.
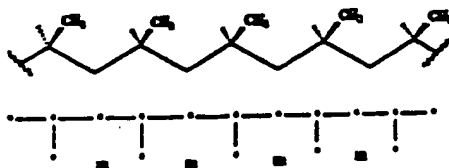
The degree of isotactic regularity may be measured by NMR
techniques. Bovey's NMR nomenclature for an isotactic
pentad is ... mmmm ... with each "m" representing a
"meso" dyad or successive methyl groups on the same side
in the plane.

In the normal isotactic structure of a polyolefin,
all of the monomer units have the same stereochemical
configuration, with the xc pti n f random err rs which
app ar al ng th polym r. Such random err rs almost
always appear as is lated inversions of configurati n
which are c rrected in the very n xt α-olefin monom r

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insertion to restore the original R or S configuration of the propagating polymer chain.

The formation of stereoblock isotactic polymer differs from the formation of the normal isotactic structure in the way that the propagation site reacts to a stereochemical error in the chain. As mentioned above, the normal isotactic chain will return to the original configuration following an error because the stereochemical regulator, the catalytic active metal species and its surrounding ligands, continues to dictate the same stereochemical preference during monomer insertion. In stereoblock propagation, the catalytically active metal site itself changes from one which dictates a monomer insertion of R configuration to one which dictates an S configuration for monomer insertion. The isotactic stereoblock form is shown below.
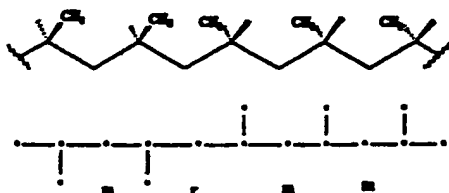
Long before anyone had discovered a catalyst system which produced the isotactic stereoblock form of a polyolefin, the possible existence of a polymer of such micro-structure had been recognized and mechanisms for its formation had been proposed based on conventional Ziegler-Natta mechanisms in Langer, A.W., Lect. Bienn. Polym. Symp. 7th (1974); Ann. N.Y. Acad. Sci. 295, 110-126 (1977). The first example of this form of polypropylene and a catalyst which produces it in a pure f rm were reported in U.S. Pat nt No. 4,522,982.

The lengths f individual bl cks f the same configuration in the ster oblock structure vary wid ly due t changing reacti n conditions. Since nly th

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erroneous parts of the chains affect the crystallinity of the resin product, in general, normal isotactic polymers and isotactic stereoblock polymers of long block length (greater than 50 isotactic placements). have similar properties.

Highly isotactic polyolefins exhibit a high degree of crystallinity. Accordingly, isotactic polyolefins are, depending upon their weight average molecular weight exceeding about 100,000, well suited to high strength end use applications.

Syndiotactic polyolefins are those wherein the hydrocarbyl groups pendent to the polymer molecular backbone alternate sequentially in order from one side or plane to the opposite side or plane relative to the polymer backbone, as shown below.
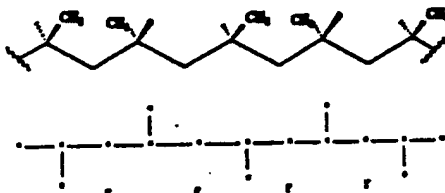
In NMR nomenclature, this segment, or pentad, is described as ... rrrr ... in which each r represents a "racemic" dyad, i.e., successive methyl groups on alternate sides of the plane. The percentage of r dyads in the chain determines the degree of syndiotacticity of the polymer. Highly syndiotactic polymers are generally highly crystalline and will frequently have high melting points similar to their isotactic polymorphs. Like isotactic polyolefins, syndiotactic polyolefins are capable f xhibiting a high degr of crystallinity, hence ar suitable for high strength applicati ns pr vid d th ir M_W exceeds about 100,000.

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For any of the above described materials the final
resin properties and its suitability for particular
applications depend on the type of tacticity, the melting
point, the average molecular weight, the molecular weight
distribution, the type and level of monomer and
comonomer, the sequence distribution, and the presence or
absence of head or end group functionality. Accordingly,
the catalyst system by which such a stereoregular
polyolefin is to be produced should, desirably, be
versatile in terms of M_w, MWD, tacticity type and level,
and comonomer choice. Further, the catalyst system
should be capable of producing these polymers with or
without head and/or end group functionality, such as
olefinic unsaturation. Still further, such catalyst
system must be capable, as a commercially practical
constraint, of producing such resins at an acceptable
production rate. Most preferably, the catalyst system
should be one which, at its productivity rate, provides
a resin product which does not require a subsequent
treatment to remove catalyst residue to a level which is
acceptable for the resin in the end use application
desired. Finally, an important feature of a commercial
catalyst system is its adaptability to a variety of
processes and conditions.

Conventional titanium based Ziegler-Natta catalysts
for the preparation of isotactic polymers are well known
in the art. These commercial catalysts are well suited
for the production of highly crystalline, high molecular
weight materials. The systems are, however, limited in
terms of molecular weight, molecular weight distribution,
and tacticity control. The fact that the conventional
catalysts contain several types f active sites furth r
limits their ability to contr 1 the comp sition
distribution in copolymerization.

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More recently a new method of producing isotactic
polymers from an alumoxane cocatalyzed, or activated,
metallocene which in its natural state has chirality
centered at the transition metal of the metallocene, was
5   reported in Ewen, J.A., J. Amer. Chem. Soc., v. 106, p.
6355 (1984) and Kaminsky, W., et al., Angew. Chem. Int.
Ed. Eng.; 24, 507-8 (1985).

Catalysts that produce isotactic polyolefins are
also disclosed in Patent No. 4,794,096. This patent
10 discloses a chiral, stereorigid metallocene catalyst
which is activated by an alumoxane cocatalyst which is
reported to polymerize olefins to isotactic polyolefin
forms. Alumoxane cocatalyzed metallocene structures
which have been reported to polymerize stereoregularly
15 are the ethylene bridged bis-indenyl and bis-tetra-
hydroindenyl titanium and zirconium (IV) catalyst. Such
catalyst systems were synthesized and studied in Wild et
al., J. Organomet. Chem. 232, 233-47 (1982), and were
later reported in Ewen and Kaminsky et al., mentioned
20 above, to polymerize α-olefins stereoregularly. Further
reported in West German Off DE 3443087A1 (1986), but
without giving experimental verification, is that the
bridge length of such stereorigid metallocenes can vary
from a C_1 to C_4 hydrocarbon and the metallocene rings can
25 be simple or bi-cyclic but must be asymmetric. In
contrast to the metallocene catalysts disclosed in U.S.
Patent No. 4,794,096 and West German Patent DE 3443087A1,
certain species of this invention are capable of
producing a highly isotactic polymer using an achiral
30 catalyst.

The use of transition metal based catalysts having
amid groups attach d to the transition metal have
rec iv d some attention in polymer r search. A process
for producing syndi tactic polystyr ne using a tris-amid
35 zirc nium catalyst is disclos d in U.S. Patent No.

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4,774,301. As taught therein, the zirconium compound may be combined with an alumoxane to produce a polymerization catalyst. A syndiotactic polymer results when vinyl aromatic monomers, which have been known to yield syndiotactic polymers generally, are polymerized by a tris-amido zirconium-alumoxane catalyst.

In European Patent 349,886, titanium having bonded thereto a saturated alkyl-substituted amido group, is reported to yield an active catalyst in the presence of alumoxane. This catalyst system is capable of producing polyethylene copolymers having a high degree of structural randomness and narrow molecular weight distribution. Also reported in EP 349,886 are references to prior amide containing Group IV-B metal catalysts for the homopolymerization of ethylene, which, when applied to copolymerization, suffer from the various disadvantages of low molecular weight product, broad molecular weight distribution and low catalytic activity.

In view of the high strength and other physical properties that make stereoregular polymers desirable in applications for which other moldable plastics are ill suited and in view of the few methods currently available for producing stereoregular polymers, there is a need for a catalyst as disclosed hereinafter for producing high molecular weight, highly isotactic polymers. It is further desirable that such a catalyst have high activity so as to allow production of a polymer which is ready to be molded and/or machined for its ultimate use without treatment for removal of contaminants (catalyst residue). It is also desirable to obtain a catalyst that is useful f r production f ethylene base polymers.

SUMMARY OF THE INVENTION

This invention disclos s an alumoxane cocatalyzed catalyst system f r th producti n of highly crystalline

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polyolefins the transition m tal component of which is a
bridged amido transition metal compound represented by
the general formula:
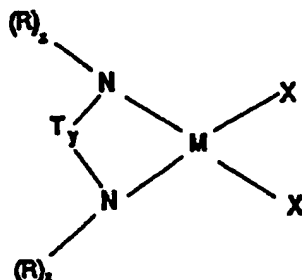
wherein: "M" is zirconium, hafnium or titanium; "N" is
a nitrogen atom having three substituents; "y" is 1 or 0
denoting the presence or absence, respectively, of a
bridging group T between nitrogen atoms and "z" is 2 - y;
"X" and "X'" are any univalent anionic ligand such as a
halide, hydride, substituted or unsubstituted C_1-C_{30}
hydrocarbyl, alkoxide, aryloxide, amide, arylamide,
phosphide, arylphosphide, or "X" and "X'" together are a
divalent radical such as an alkylidene, cyclometallated
hydrocarbyl or any other divalent anionic chelating
ligand; "T" is a covalent bridging group selected from
the group consisting of unsubstituted hydrocarbyls and
hydrocarbyls containing a Group IV-A or VI-A element; and
each "R" and "R'" is independently a radical selected
from the group consisting of singly branched hydrocarbyl
radicals having between 1 and 30 carbon atoms, multiple
branched hydrocarbyl radicals having between 1 and 30
carbon atoms, halogen radicals, amido radicals, phosphido
radicals, silyl radicals, alkoxy radicals, alkylborido
radicals, C_1-C_{30} hydrocarbyl-substituted Group IV-A
m tall id radicals; and substituted C_1-C_{30} hydrocarbyl
radicals wherein n or more hydr gen atoms is replaced
by a halogen radical, an amido radical, a phosphido
radical, an alk xy radical or any other radical
containing a Lewis acidic r basic functi nality.

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Further disclosed is a polymerization process incorporating the catalyst system. The catalyst system is prepared by the combination of an amido transition metal compound and an alumoxane, and may be employed in solution, slurry, gas phase, or high pressure polymerization. The catalyst may also be prepared in the supported form. The catalyst system of this invention polymerizes propylene to high molecular weight, highly isotactic polypropylene, in addition to homopolymerizing ethylene and copolymerizing ethylene or propylene with α-olefins, cyclic olefins, dienes or other unsaturated monomers.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A.   Transition Metal Component

The Group IV-B transition metal component of the catalyst system is represented by the general formula:
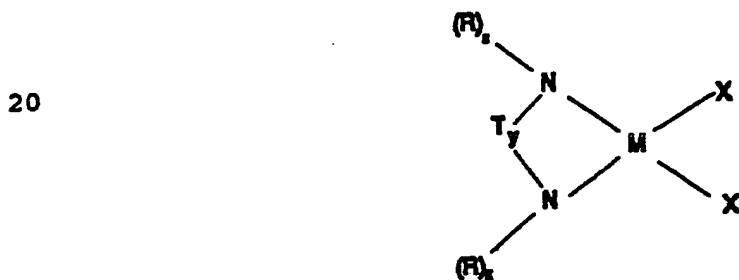
wherein the letter symbols have the following meanings:

"M" is zirconium, titanium or hafnium;

"N" is a nitrogen atom having three substituent groups;

"y" is 1 or 0 denoting the presence or absence, respectively, f a bridging group T between nitrogen atoms and "z" is 2 - y;

each "R" is ind pendently a radical selected from the group consisting of singly branched hydrocarbyl

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radicals having between 1 and 30 carbon atoms, preferrably between 3 and 30 carbon atoms; multiply branched hydrocarbyl radicals having between 1 and 30 carbon atoms, preferably between 3 and 30 carbon atoms; halogen radicals; amido radicals; phosphido radicals; silyl radicals; alkoxy; and alkylborido radicals; substituted C_1-C_{30} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical or any other radical containing a Lewis acidic or basic functionality; C_1-C_{30} hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV-A of the Periodic Table of Elements;

each "X" is independently any univalent anionic ligand such as a halide, hydride, or substituted or unsubstituted C_1-C_{20} hydrocarbyl, alkoxide, aryloxide, amide, arylamide, phosphide, arylphosphide or both "X" and "X'" together are an alkylidene, a cyclometallated hydrocarbyl or any other divalent anionic chelating ligand; more particularly, X may be a ligand of the general formula $N(R)_2$ wherein R has the same meaning previously ascribed to it; most particularly, X may be a silylamide of the general formula $N[Si(R)_3]_2$;

T is a covalent bridging group containing a Group IV-A or VI-A element such as, but not limited to, a dialkyl, alkylaryl or diaryl silicon radical; a dialkyl, alkylaryl or diaryl germanium radical; alkyl or aryl phosphine; alkyl or aryl amine radical; an oxygen or sulfur radical; or a hydrocarbyl radical having 1 or more carbon atoms such as methylene, ethylene and the like.

Specific, nonlimiting examples of the T group which are suitable as a constituent group of the Group IV-B transition metal component f th catalyst system are dimethylsilyl, di thylsilyl, di-n-propylsilyl, diisopr pylsilyl, di-n-butylsilyl, di-t-butylsilyl, di-n-

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hexylsilyl, methylphenylsilyl, ethylmethylsilyl, diphenylsilyl, di(p-t-butylphenethylsilyl), n-hexylmethylsilyl, cyclopentamethylenesilyl, cyclotetramethylenesilyl, cyclotrimethylenesilyl, dimethylgermanyl, diethylgermanyl, methylene, dimethylmethylene, diethylmethylene, ethylene, dimethylethylene, diethylethylene, dipropylethylene, propylene, dimethylpropylene, diethylpropylene, 1,1-dimethyl3-3-dimethylpropylene, tetramethyldisiloxane, 1,1,4,4-tetramethyldisilylethylene, oxygen and sulfur.

Exemplary hydrocarbyl radicals for X are methyl, ethyl, propyl, isopropyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl and the like, with methyl being preferred. Exemplary halogen atoms for X include chlorine, bromine, fluorine and iodine, with chlorine being preferred. Exemplary alkoxides and aryloxides for X are methoxide, ethoxide, propoxide, butoxide, phenoxide and substituted phenoxides such as 4-methylphenoxide. Exemplary amides of X are dimethylamide, diethylamide, methylethylamide, di-t-butylamide, diisoproylamide and the like. Exemplary aryl amides are diphenylamide and any other substituted phenyl amides. Exemplary silyl amides are di-trimethylsilylamide, di-triethylsilylamide and triethyl-trimethyl silylamide, with di-trimethylsilylamide being preferred. Exemplary phosphides of X are diphenylphosphide, dicyclohexylphosphide, diethylphosphide, dimethylphosphide and the like. Exemplary alkyldiene radicals for both X's together are methylidene, ethylidene, propylidene, or the dianion of ethyleneglycol and the like.

Suitable hydr carbyl and substituted hydrocarbyl radicals f r th R gr up will c ntain from 1 t about 30 carbon at ms and include singly and multiply branched

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alkyl radicals, cyclic hydrocarbon radicals, alkyl-
substituted cyclic hydrocarbon radicals, aromatic
radicals and alkyl-substituted aromatic radicals, amido-
substituted hydrocarbon radicals, phosphido-substituted
5   hydrocarbon radicals, alkoxy-substituted hydrocarbon
radicals, and halo-substituted hydrocarbon radicals or
hydrocarbon radicals containing substitutions by any
Lewis basic or acidic functional group. Suitable
organometallic radicals for the R group include
10   trimethylsilyl,   triphenylsilyl,   triphenylgermyl,
trimethylgermyl and the like. Other suitable radicals
for the R group include amido radicals, phosphido
radicals, alkoxy radicals, alkyl boride radicals and the
like.   Of the suitable R groups the organometalic
15   radicals   of   silicon   such   as   trimethylsilyl,
triethylsilyl, ethyldimethylsilyl and methyldiethylsilyl
are preferred; the most preferred being trimethylsilyl.

A number of final components may be formed by
permuting all possible combinations of the constituent
20   moieties with each other. Illustrative transition metal
compounds are: bis(di-trimethylsilylamido) zirconium
dichloride,   bis(di-isobutylamido)   hafnium   dimethyl,
bis(di-tertbutylamido)zirconium   dichloride,   (di-
cyclohexylamido)(di-trimethylsilylamido)   titanium
25   dihydride,   tris(di-trimethylsilylamido)   zirconium
chloride, tris(di-triphenylgermylamido) hafnium chloride,
and tetrakis(di-trimethylsilylamido) zirconium.

The Group IV-B metal compounds have been used to
produce isotactic polypropylene of high stereoregularity.
30   As demonstrated in example 9, when the achiral compound
bis(di-trimethylsilylamido) zirconium dichloride is
combined with alumoxane to form a catalyst system, that
system is capable of producing isotactic polypropyl ne
having fewer than 50 chain d f cts p r 1000 monomer
35   units. The preparation of compounds of this typ are

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well known in the literature and include references such
as R.A. Anderson, _Inorganic Chemistry_ (1979), 18, 2928.

B.   Alumoxane Component

The alumoxane component of the catalyst system is an
oligomeric compound which may be represented by the
general formula $(R^3-Al-O)_m$ which is a cyclic compound, or
may be $R^4(R^5-Al-O-)_m-AlR^6_2$ which is a linear compound.
An alumoxane is generally a mixture of both the linear
and cyclic compounds. In the general alumoxane formula
R^3, R^4, R^5 and R^6 are, independently a C_1-C_5 alkyl
radical, for example, methyl, ethyl, propyl, butyl or
pentyl and "m" is an integer from 1 to about 50. Most
preferably, R^3, R^4, R^5 and R^6 are each methyl and "m" is
at least 4. When an alkyl aluminum halide is employed in
the preparation of the alumoxane, one or more R^{3-6} groups
may be halide.

As is now well known, alumoxanes can be prepared by
various procedures. For example, a trialkyl aluminum may
be reacted with water, in the form of a moist inert
organic solvent; or the trialkyl aluminum may be
contacted with a hydrated salt, such as hydrated copper
sulfate suspended in an inert organic solvent, to yield
an alumoxane. Generally, however prepared, the reaction
of a trialkyl aluminum with a limited amount of water
yields a mixture of both linear and cyclic species of
alumoxane.

Suitable alumoxanes which may be utilized in the
catalyst systems of this invention are those prepared by
the   hydrolysis   of   a   trialkylaluminum   or
haloalkylaluminum;   such   as   trimethylaluminum,
tri thylaluminum, tripropylaluminum; triis butylaluminum,
dimethylaluminumchl ride,   diis butylaluminumchloride,
di thylaluminumchlorid , and the like. The m st pr ferr d
alum xane f r us is m thylalum xan   (MAO).

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Methylalumoxanes having an average degree f
oligomerization of from about 4 to about 25 ("m" = 4 to
25), with a range of 13 to 25, are the most preferred.

5   C.   Catalyst System

The catalyst systems employed in the invention
comprise a complex formed upon admixture of the amido
Group IV-B transition metal component with an alumoxane
component. The catalyst system may be prepared by
10   addition of the requisite bis-amido Group IV-B transition
metal and alumoxane components to an inert solvent in
which olefin polymerization can be carried out by a
solution, slurry or bulk phase polymerization procedure.

The catalyst system may be conveniently prepared by
15   placing the selected amido Group IV-B transition metal
component and the selected alumoxane component, in any
order of addition, in an alkane or aromatic hydrocarbon
solvent -- preferably one which is also suitable for
service as a polymerization diluent. Where the
20   hydrocarbon solvent utilized is also suitable for use as
a polymerization diluent, the catalyst system may be
prepared in situ in the polymerization reactor.
Alternatively, the catalyst system may be separately
prepared, in concentrated form, and added to the
25   polymerization diluent in a reactor. Or, if desired, the
components of the catalyst system may be prepared as
separate solutions and added to the polymerization
diluent in a reactor, in appropriate ratios, as is
suitable for a continuous liquid phase polymerization
30   reaction procedure. Alkane and aromatic hydrocarbons
suitable as solvents for formation of the catalyst system
and also as a polymerization diluent are exemplified by,
but ar n t necessarily limited to, straight and branched
chain hydrocarbons such as is butan , butane, pentane,
35   hexane, h ptane, octan and the like, cyclic and

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alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane and the like, and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene and the like. Suitable solvents

5   also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, 1-butene, 1-hexene and the like.

In accordance with this invention optimum results are generally obtained wherein the amido Group IV-B

10   transition metal compound is present in the polymerization diluent in a concentration of from about 0.0001 to about 1.0 millimoles/liter of diluent and the alumoxane component is present in an amount to provide a molar aluminum to transition metal ratio of from about

15   1:1 to about 20,000:1. Sufficient solvent should be employed so as to provide adequate heat transfer away from the catalyst components during reaction and to permit good mixing.

The catalyst system ingredients -- that is, the

20   amido Group IV-B transition metal, the alumoxane, and polymerization diluent -- can be added to the reaction vessel rapidly or slowly. The temperature maintained during the contact of the catalyst components can vary widely, such as, for example, from -10° to 300°C. Greater

25   or lesser temperatures can also be employed. Preferably, during formation of the catalyst system, the reaction is maintained within a temperature of from about 25° to 100°C, most preferably about 25°C.

At all times, the individual catalyst system

30   components, as well as the catalyst system once formed, are protected from oxygen and moisture. Therefore, the r actions to pr pare the catalyst system are p rformed in an xygen and moisture fr atmosph r and, where th catalyst system is r c ver d s parately it is r covered

35   in an xygen and moisture fre atm sph r . Preferably,

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therefore, the reactions are performed in the presence of an inert dry gas such as, for example, helium or nitrogen.

5   D.   Polymerization Process

In a preferred embodiment of the process of this invention the catalyst system is utilized in the liquid phase (slurry, solution, suspension or bulk phase or combination thereof), high pressure fluid phase or gas

10   phase polymerization of an olefin monomer. These processes may be employed singularly or in series. The liquid phase process comprises the steps of contacting an olefin monomer with the catalyst system in a suitable polymerization diluent and reacting said monomer in the

15   presence of said catalyst system for a time and at a temperature sufficient to produce a polyolefin of high molecular weight.

The monomer for such process may comprise propylene alone, for the production of a isotactic polypropylene.

20   Conditions most preferred for the production of isotactic polypropylene are those wherein propylene is submitted to the reaction zone at pressures of from about 0.019 psi to about 50,000 psi and the reaction temperature is maintained at from about -100° to about 300°C. The

25   aluminum to transition metal molar ratio is preferably from about 1:1 to 20,000:1. A more preferable range would be 1:1 to 2000:1. The reaction time is preferably from about 1 hour to about 6 hours.

The monomer may also comprise ethylene alone, for

30   the production of homopolyethylene, or ethylene in combination with an α-olefin having 3 to 20 carbon atoms for the production of an ethylene-α-olefin copolymer. Homopolymers of high r α-olefin such as but ne and copolym rs thereof with thylene and/or C_4 r higher

35   α- l fins and di lefins can also be pr par d. C nditions

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most preferred for the homo- or copolymerization of ethylene are those wherein ethylene is submitted to the reaction zone at pressures of from about 0.019 psi to about 50,000 psi and the reaction temperature is maintained at from about -100° to about 300°C. The aluminum to transition metal molar ratio is preferably from about 1:1 to 20,000:1. A more preferable range would be 1:1 to 2000:1. The reaction time is preferably from about 10 seconds to about 1 hour.

Without limiting in any way the scope of the invention, one means for carrying out the process of the present invention for production of a copolymer is as follows: in a stirred-tank reactor, liquid α-olefin monomer is introduced, such as 1-butene. The catalyst system is introduced via nozzles in either the vapor or liquid phase. Feed ethylene gas is introduced either into the vapor phase of the reactor, or sparged into the liquid phase as is well known in the art. The reactor contains a liquid phase composed substantially of liquid α-olefin comonomer, together with dissolved ethylene gas, and a vapor phase containing vapors of all monomers. The reactor temperature and pressure may be controlled via reflux of vaporizing α-olefin monomer (autorefrigeration), as well as by cooling coils, jackets etc. The polymerization rate is controlled by the concentration of catalyst. The ethylene content of the polymer product is determined by the ratio of ethylene to α-olefin comonomer in the reactor, which is controlled by manipulating the relative feed rates of these components to the reactor.

EXAMPLES

Example 1

Th polymerization run was performed in a 1-liter autoclav react r quipped with a paddl stirr r, an

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external water jacket for temperature control, a
regulated supply of dry nitrogen, ethylene, propylene,
1-butene and hexane, and a septum inlet for introduction
of other solvents or comonomers, transition metal
5   compound and alumoxane solutions. The reactor was dried
and degassed thoroughly prior to use. A typical run
consisted of injecting 400 ml of toluene, 5 ml 1.0 M MAO,
0.27 mg of [(Me$_3$Si)$_2$N]$_2$ZrCl$_2$ (0.2 ml of a 13.5 mg in
10 ml of toluene solution) into the reactor. The reactor
10   was then heated to 80°C and the ethylene (60 psi) was
introduced into the system. The polymerization reaction
was limited to 10 minutes. The reaction was ceased by
rapidly cooling and venting the system. The solvent was
evaporated off of the polymer by a stream of nitrogen.
15   Polyethylene was recovered (7.4 g, MW = 315,000, MWD =
2.261).

Example 2

Using the same reactor design and general procedure
as example 1, 400 ml of toluene, 5.0 ml of 1.0 M MAO, and
20   0.32 mg of [(Me$_3$Si)$_2$N]$_2$HfCl$_2$ (0.2 ml of a 1.60 mg in
10 ml of toluene solution) were added to the reactor.
The reactor was heated at 80°C, the ethylene was
introduced (60 psi), and the reaction was allowed to run
for 10 minutes, followed by rapidly cooling and venting
25   the system. After evaporation of the toluene, 2.7 g of
polyethylene was recovered (MW = 267,200, MWD = 2.122).

Example 3

Using the same reactor design and general procedure
as example 1, 300 ml of toluene, 100 ml of propylene, 7.0
30   ml of 1.0 M MAO, and 1.35 mg of [(Me$_3$Si)$_2$N]$_2$ZrCl$_2$ (1 ml
of a 13.5 mg in 10 ml of toluene solution) were added to
the reactor. The reactor was heated at 50°C, the
ethylene was introduc d (65 psi), and the r action was
all wed t run f r 30 minutes, followed by rapidly
35   cooling and venting the system. After evaporation of the

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toluene, 9.3 g of an ethylene-propylene copolymer was recovered (MW = 131,000, MWD = 1.837, 121.7 short chain branches (SCB)/1000C by IR).

Example 4

5   Using the same reactor design and general procedure as example 1, 300 ml of toluene, 100 ml of propylene, 7.0 ml of 1.0 M MAO, and 1.6 mg of [(Me$_3$Si)$_2$N]$_2$HfCl$_2$ (1 ml of a 16 mg in 10 ml of toluene solution) were added to the reactor. The reactor was heated at 80°C, the ethylene
10   was introduced (60 psi), and the reaction was allowed to run for 30 minutes, followed by rapidly cooling and venting the system. After evaporation of the toluene, 8.2 g of an ethylene-propylene copolymer was recovered (MW = 80,700, MWD = 1.537, 89.3 SCB/1000C by IR).

15   Example 5

Using the same reactor design and general procedure as example 1, 300 ml of toluene, 100 ml of 1-butene, 7.0 ml of 1.0 M MAO, and 1.35 mg of [(Me$_3$Si)$_2$N]$_2$ZrCl$_2$ (1 ml of a 13.5 mg in 10 ml of toluene solution) were added to
20   the reactor. The reactor was heated at 80°C, the ethylene was introduced (60 psi), and the reaction was allowed to run for 30 minutes, followed by rapidly cooling and venting the system. After evaporation of the toluene, 4.3 g of an ethylene-butene copolymer was
25   recovered (MW = 91,100, MWD = 1.643, 51.4 SCB/1000C by ^{13}C NMR).

Example 6

Using the same reactor design and general procedure as example 1, 300 ml of toluene, 100 ml of 1-butene, 7.0
30   ml of 1.0 M MAO, and 1.6 mg of [(Me$_3$Si)$_2$N]$_2$HfCl$_2$ (1 ml of a 16 mg of 10 ml of toluene solution) were added to the reactor. The reactor was heated at 80°C, the ethylene was introduced (60 psi), and the reaction was all w d to run f r 30 minutes, foll w d by rapidly c oling and
35   venting the system. After evaporation f the toluen ,

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9.3 g of an ethylene-butene copolymer was recovered (MW = 70,800, MWD = 1.710, 46.8 SCB/1000C by ^{13}C NMR).

Example 7

Using the same reactor design and general procedure as example 1, 300 ml of toluene, 100 ml of 1-hexene, 7.0 ml of 1.0 M MAO, and 1.35 mg of $[(Me_3Si)_2N]_2ZrCl_2$ (1 ml of a 13.5 mg in 10 ml of toluene solution) were added to the reactor. The reactor was heated at 80°C, the ethylene was introduced (60 psi), and the reaction was allowed to run for 30 minutes, followed by rapidly cooling and venting the system. After evaporation of the toluene, 13.9 g of an ethylene-hexene copolymer was recovered (MW = 111,200, MWD = 1.782, 32.2 SCB/1000C by IR).

Example 8

Using the same reactor design and general procedure as example 1, 300 ml of toluene, 100 ml of 1-hexene, 7.0 ml of 1.0 M MAO, and 1.6 mg of $[(Me_3Si)_2N]_2HfCl_2$ (1 ml of a 16.0 mg in 10 ml of toluene solution) were added to the reactor. The reactor was heated at 50°C, the ethylene was introduced (65 psi), and the reaction was allowed to run for 30 minutes, followed by rapidly cooling and venting the system. After evaporation of the toluene, 8.7 g of an ethylene-hexene copolymer was recovered (MW = 236,700, MWD = 1.780, 20.1 SCB/1000C by IR).

Example 9

Using the same reactor design and general procedure as example 1, 100 ml of toluene, 200 ml of propylene, 10.0 ml of 1.0 M MAO, and 8.3 mg of $[(Me_3Si)_2N]_2ZrCl_2$ in 10 ml toluene were added to the reactor. The reactor was heated at 30°C and the reaction was allowed to run for 3 hours, followed by rapidly cooling and venting the system. After evaporation of the t luene, 3.2 g of isotactic p lypr pyl ne was recovered (MW = 95,500, MWD =

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1.758, 90% (m) isotactic with 40 chain defects per 1000 monomer units as determined by ^{13}C NMR, 146°C mp).

Example 10

The polymerization was performed in a stirred 100 ml stainless steel autoclave which was equipped to perform polymerizations at temperatures up to 300°C and pressures up to 2500 bar. the reactor was evacuated, purged with nitrogen, purged with ethylene and heated to 202°C. The comonomer, 1-hexene (75 ml), was added to the reactor under ethylene pressure. A stock solution of $[(Me_3Si)_2N]_2ZrCl_2$ was prepared by dissolving 7.6 mg of the transition metal compound in 25 ml of toluene. The test solution was prepared by adding 2.5 ml of the stock solution to 10.0 ml of a 1.0 M MAO solution. The test solution (0.43 ml) was transferred by nitrogen pressure into a constant-volume injection tube. The autoclave was pressurized with ethylene to 1792 bar and was stirred at 1800 rpm. The test solution (0.43 ml) was injected into the autoclave with excess pressure, at which time a temperature rise of 9°C was observed. The temperature and pressure were recorded continuously for 120 seconds, at which time the contents of the autoclave were rapidly vented into a receiving vessel. The reactor was washed with xylene to recover any polymer remaining within. These washings were combined with the polymer released when the reactor was vented. Precipitation of the polymer from the mixture by addition of acetone yielded 1.3 g of an ethylene-hexene copolymer (MW = 42,000, MWD = 2.07, 8.9 SCB/1000C by IR).

Example 11

Using the same reactor design as described in example 10, the reactor was evacuated, purged with nitrogen, purg d with ethylene and h at d t 199°C. The comon mer 1-hexen (75 ml), was added to the reactor und r ethylen pressur. A st ck solution f

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[(Me$_3$Si)$_2$N]$_2$HfCl$_2$ was prepared by dissolving 9.0 mg of the transition metal compound in 25 ml of toluene. The test solution was prepared by adding 2.5 ml of the stock solution to 10.0 ml of a 1.0 M MAO solution. The test solution (0.43 ml) was transferred by nitrogen pressure into a constant-volume injection tube. The autoclave was pressurized with ethylene to 1831 bar and was stirred at 1800 rpm. The test solution was injected into the autoclave with excess pressure, at which time a temperature rise of 7°C was observed. The temperature and pressure were recorded continuously for 120 seconds, at which time the contents of the autoclave were rapidly vented into a received vessel. The reactor was washed with xylene to recover any polymer remaining within. These washings were combined with the polymer released when the reactor was vented. Precipitation of the polymer from the mixture by addition of acetone yielded 0.5 g of an ethylene-hexene copolymer (MW = 57,000, MWD = 2.22, 8.0 SCB/1000C by IR).

TABLE A

EXAMPLE NUMBER	COMPOUND[a]		CATALYST		REACTOR				POLYMER PRODUCT		
	TRANSITION METAL	TRANSITION METAL COMPOUND ("TMC") (μ moles)	ALUMOXANE ("MAO") (μ moles)	CATALYTIC EFFICIENCY (g POLYMER/μ mole TMC)	MONOMER/COMONOMER	ETHYLENE PRESSURE (PSI)	TEMPERATURE (°C)	YIELD (g)	MOLECULAR WEIGHT (g/mole)	MOLECULAR WEIGHT DISTRIBUTION	SCB/1000 °C
1	Zr	0.56	5000	13.2	ETHYLENE	60	80	7.4	315,100	2.261	---
2	Hf	0.56	5000	4.8	ETHYLENE	60	80	2.4	267,200	2.122	---
3	Zr	7 81	7000	3.3	ETHYLENE/PROPYLENE	60	50	9.3	131,100	1.837	121.7[d]
4	Hf	2.81	7000	2.9	ETHYLENE/PROPYLENE	60	80	8.2	80,700	1.537	89.3[d]
5	Zr	2.81	7000	1.5	ETHYLENE/1-BUTENE	60	80	4.3	91,100	1.643	51.4[c]
6	Hf	2.81	7000	3.3	ETHYLENE/1-BUTENE	60	80	9.3	70,800	1.710	46.8[c]
7	Zr	2.81	7000	4.9	ETHYLENE/1-HEXENE	60	80	13.9	111,200	1.782	32.2[c]
8	Hf	2.81	7000	3.1	ETHYLENE/1-HEXENE	65	50	8.7	236,700	1.780	20.0[d]
9	Zr	17.3	10000	0.2	PROPYLENE	---	30	3.2[b]	95,500	1.758	---
10	Zr	1.58	4300	0.8	ETHYLENE/1-HEXENE	2.6x10⁴	202	1.3	42,000	2.07	8.9[d]
11	Hf	1.56	4300	0.3	ETHYLENE/1-HEXENE	2.7x10⁴	199	0.5	51,000	2.22	8.0[d]

a   The transition metal catalyst components of the examples are zirconium and hafnium species of $[(Me_3)Si)_2N]_2MCl_2$.
b   90% isotactic polypropylene having 40 defects per 1000 monomer units (determined by ^{13}C NMR) was produced.
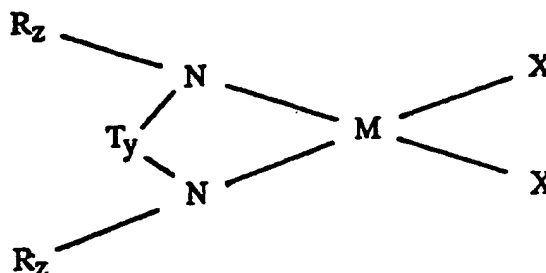c   Determined by ^{13}C NMR.
d   Determined by IR.

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The invention has been described with reference to its preferred embodiments. Those of ordinary skill in the art may, upon reading this disclosure, appreciate
5 changes or modifications which do not depart from the scope and spirit of the invention as described above or claimed hereafter.
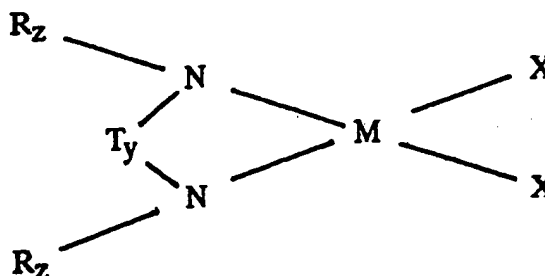
<u>Claims:</u>

A compound represented by the general formula:

$$R_z - N \diagdown \diagup T_y \diagdown N - R_z \diagdown \diagup M \diagup X \diagdown X$$

wherein: "y" is 1 denoting the presence of a bridging group T between nitrogen atoms; "z" is 2 - y; "M" is zirconium, hafnium or titanium; "N" is a nitrogen atom having three substituents; each "X" is, independently, any univalent anionic ligand such as a halide, hydride, substituted or unsubstituted C_1-C_{30} hydrocarbyl, alkoxide, aryloxide, amide, arylamide, phosphide, or arylphosphide; "T" is a covalent bridging group selected from the group consisting of unsubstituted hydrocarbyls and substituted hydrocarbyls containing a Group IV-A or VI-A element; and each "R" is, independently, a radical selected from the group consisting of singly branched hydrocarbyl radicals having between 4 and 30 carbon atoms, multiply branched hydrocarbyl radicals having between 4 and 30 carbon atoms, halogen radicals, amido radicals, phosphido radicals, silyl radicals, alkoxy radicals, alkylborido radicals, C_1-C_{30} hydrocarbyl-substituted Group IV-A metalloid radicals; and substituted C_1-C_{30} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amino radical, a phosphido radical, an alkoxy radical or any other radical containing a Lewis acidic or basic functionality.

2. A catalyst system for the polymerization of alpha olefins comprising:

a) The compound of claim 1 or a compound of the general formula:

$$R_z - N \diagdown \diagup T_y \diagdown N - R_z \diagdown \diagup M \diagup X \diagdown X$$

wherein: "y" is 1 r 0 denoting the presence or absence, respectively, of a bridging group T between nitrogen atoms; "z" is 2 - y; "M" is zirconium, hafnium, or titanium; "N" is a nitrogen atom having three substituents; each "X" is, independently, any univalent anionic ligand such as a halide, hydride, substituted or unsubstituted C_1-C_{30} hydrocarbyl, alkoxide, aryloxide, amide, arylamide, phosphide or arylphosphide; "T" is a covalent bridging group selected from the group consisting of unsubstituted hydrocarbyls and substituted hydrocarbyls containing a Group IV-A or VI-A element; and each "R" is, independently, a radical selected from the group consisting of singly branched hydrocarbyl radicals having between 4 and 30 carbon atoms, multiply branched hydrocarbyl radicals having between 4 and 30 carbon atoms, halogen radicals, amido radicals, phosphido radicals, silyl radicals, alkoxy radicals, alkylborido radicals, C_1-C_{30} hydrocarbyl-substituted Group IV-A metalloid radicals; and substituted C_1-C_{30} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical or any other radical containing a Lewis acidic or basic functionality; and

b) an alumoxane.

3. The compound of claim 1 or system of claim 2 wherein each R is, independently, a radical selected from the group consisting of halogen radicals, amido radicals, phosphido radicals, silyl radicals, alkoxy radicals, alkylborido radicals, C_1-C_{30} hydrocarbyl-substituted Group IV-A metalloid radicals; and substituted C_1-C_{30} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical or any other radical containing a Lewis acidic or basic functionality.

4. The compound or system of claim 1, 2, or 3 wherein "T" is a covalent bridging group containing a Group IV-A atom.

5. The compound or system of any preceding claim wherein at least one "R" is a silicon containing radical.

6. The compound or system of any preceding claim wherein at least one "X" is a nitrogen containing radical.

7. The compound or system of any preceding claim wherein each "X" is, independently, selected from the group consisting of hydrides, alkoxides, amides, hydrocarbyls and halides.

8. The compound or system of claim 7 wherein at least one "X" is selected from the group consisting of hydrides, hydrocarbyls, amidos, and halides.

9. The compound or system of any preceding claim wherein "M" is zirconium or hafnium.

10. The catalyst system of any of claims 2-11 wherein the alumoxane is derived from the hydrolysis of an aluminumalkyl selected from the group consisting of trimethylaluminum, triethylaluminum, and triisobutylaluminum.

11. The catalyst system of any of claims 2-15 wherein the aluminum:transition metal ratio is from 1:1 to 20,000:1.

12. A process for producing poly alpha-olefin comprising the steps of:

a) contacting alpha-olefin monomer or monomers with a catalytically active combination comprising the compound or system of any preceding claim, and

b) recovering poly alpha-olefin.

13. The process of claim 12 wherein the poly alpha-olefin produced is isotactic polypropylene, the monomer of a) is propylene.

14. The process of claim 12 wherein the poly alpha-olefin produced is polyethylene or a copolymer of ethylene and another alpha-olefin having 3-20 carbon atoms, the monomer of a) comprising ethylene or ethylene and another alpha-olefin having 3 to 20 carbon atoms.

15. The process of claim 12, 13, r 14 wherein the polymerization reaction time is between 1 and 6 hours and/or the reaction

pressure is from 0.13 kPa (0.019 psi) to 344.75 MPa (50,000 psi) and/or the reaction temperature is maintained between -100° C and 300° C.

16. The process of claim 15 wherein the polymer produced has MWD in the range of 1.5-3.

17. The process of claim 15 or 16 wherein the polymer produced has SCB in the range of 5-150.

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: C 07 F 7/00, C 08 F 4/642, C 08 F 10/00

II. FIELDS SEARCHE

Minimum Documentation Searched

Classification System	Classification Symbols
IPC⁵	C 07 F, C 08 F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	ORGANOMETALLICS, vol. 2, no. 1, January 1983, pages 16-20, R.P. PLANALP et al. "Dialkyl Bis(bis(trimethylsilyl)amido) Group 4A Metal Complexes", see pages 19-20, Experimental Section. --	1
X	ZEITSCHRIFT FÜR ANORGANISCHE UND ALLGEMEINE CHEMIE, vol. 459, December 1979, pages 111-118, H. BÜRGER, D. BEIERSDORF "Cyclische Titanamide mit Sila-titana--diazacyclobutan-Struktur", see page 118, table 3. --	1
X	JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 192, 1980, pages 189-193, R.A. ANDERSEN "Dialkylbis(bis(trimethyl-	1

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

01 April 1992

Date of Mailing of this International Search Report

16. 04. 92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

Danielle van der Haas

International Application No PCT/US 91/09676

Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	silyl)amido)hafnium(IV); Unsymmetrical Dialkyl and Alkyloxide Derivatives", see pages 190-193, Experimental. --	
X	INORGANIC CHEMISTRY, vol. 18, December 1979, pages 2928-2932, R.A. ANDERSEN "Dialkylbis(bis(trimethyl-silyl)amido)zirconium(IV) and -hafnium(IV).", see page 2931, Experimental Section. --	1
A	US, A, 4 774 301 (CAMPBELL Jr. et al.) 27 September 1988 (27.09.88), see claim 1. ----	2

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

zum internationalen Recherchen-bericht über die internationale Patentanmeldung Nr.	to the International Search Report to the International Patent Application No.	au rapport de recherche inter-national relatif á la demande de brevet international n°

PCT/US 91/09676 SAE 55987

In diesem Anhang sind die Mitglieder der Patentfamilien der im obenge-nannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unter-richtung und erfolgen ohne Gewähr.	This Annex lists the patent family members relating to the patent documents cited in the above-mentioned inter-national search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.	La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche inter-national visée ci-dessus. Les reseigne-ments fournis sont donnés á titre indica-tif et n'engagent pas la responsibilité de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US A 4774301	27-09-88	keine - none - rien	